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Novel platinum black electroplating technique improving mechanical stability

Raeyoung Kim and Yoonkey Nam, *Member, IEEE*

Abstract— **Platinum black microelectrodes are widely used as an effective neural signal recording sensor. The simple fabrication process, high quality signal recording and proper biocompatibility are the main advantages of platinum black microelectrodes. When microelectrodes are exposed to actual biological system, various physical stimuli are applied. However, the porous structure of platinum black is vulnerable to external stimuli and destroyed easily. The impedance level of the microelectrode increases when the microelectrodes are damaged resulting in decreased recording performance. In this study, we developed mechanically stable platinum black microelectrodes by adding polydopamine. The polydopamine layer was added between the platinum black structures by electrodeposition method. The initial impedance level of platinum black only microelectrodes and polydopamine added microelectrodes were similar but after applying ultrasonication the impedance value dramatically increased for platinum black only microelectrodes, whereas polydopamine added microelectrodes showed little increase which were nearly retained initial values. Polydopamine added platinum black microelectrodes are expected to extend the availability as neural sensors.**

I. Introduction

Microelectrodes have long been used as a neural signal sensor to study the electrical activities of neural networks [1,2]. Since the size of the microelectrodes is in micro scale, highly specific signal recording is possible. Microelectrode array (MEA) is a convenient platform for multiple signal recordings with high specificity. MEAs provide massive neural signal data effectively so they are widely used to various applications such as biosensors, drug screening and neuroprosthetics [1,3–5].

To acquire high quality of neural signals the electrical characteristics of the microelectrodes is important [5,6]. The electrical characteristic is usually analyzed through electrode-electrolyte impedance which is highly related to recording performance of electrodes. The lower impedance becomes, the lower background noise occurs. The neural signals, which are in micro-volt scale, can be easily classified when the background noise level is low enough. Electrode-electrolyte impedance is related to the surface area of an electrode. Impedance is reduced when the surface area is increased, but microelectrodes are not able to achieve large surface area. The breakthrough is the construction of nanostructures on the surface of the microelectrodes which supplying a large effective surface area within a restricted geometrical area of the microelectrodes. Various materials have been applied to develop nanostructures and platinum black is one of the most representative materials that are used as neural electrodes [7–11]. They have low enough impedance values for neural sensor because of their porous structure. In addition, simple and easy fabrication process and biocompatibility are other advantages of platinum black microelectrodes.

Even though the platinum black microelectrodes have excellent electrical properties as neural sensors, the porous structure is very delicate that it is broken easily to the external stimuli [12]. This can be a critical problem because the electrical property is directly related to the porous structure. MEAs are often exposed to physical stimuli during washing and sterilizing process for cell culture. The initial impedance values of MEAs are changed when the porous structures are destroyed resulting in reduced electrical performance.

In this study, we fabricated a mechanically stable neural sensor by electrochemical deposition of polydopamine. Polydopamine is famous for its strong adhesion to universal materials [13]. It has been utilized in various applications such as biosensors, nanoparticle fabrication and cell patterning [14–17]. Recently, area specific polydopamine layer deposition was demonstrated through electrochemical deposition [18]. By applying this method, the polydopamine layers were added between the platinum black structures. We compare the electrical properties of the polydopamine added platinum black (pDA-PtBK) microelectrodes and platinum black only (PtBK) microelectrodes after exposing ultrasonication environment. We confirmed that pDA-PtBK microelectrodes are more mechanically stable compare to PtBK microelectrodes.

II. Materials and Methods

A. MEA fabrication

MEA was fabricated by combining mini-MEA and printed circuit board (PCB) packaging. The mini-MEA consisted of microelectrodes for neural signal sensing, pads for PCB packaging and connection lines for microelectrodes and pads. The mini-MEA was fabricated through photolithography process. On a glass wafer, the pattern of microelectrodes, pads and lines were transferred as a 200 nm-thick gold film layer. Then, a 500 nm-thick silicon nitride film was deposited onto the gold pattern for insulation. The partial insulation layer was removed to open the area of microelectrodes and pads. The size of microelectrodes was 50 μm in diameter. The mini-MEA was connected to a PCB by gold wiring bonding and epoxy encapsulation. The PCB was designed to fit perfectly to a commercially available amplifier.

R. Kim and Y. Nam are now with the Department of Bio and Brain Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, 305- 701, Korea (e-mail: ynam@kaist.ac.kr).

B. Electrochemical deposition

The platinum black and polydopamine were electrochemically deposited to gold microelectrodes on MEA. The two materials were deposited layer-by-layer by alternately switching electrolyte solutions. A two-electrode system was used for electrochemical deposition. A mixture of 0.1% $PtCl_6H_2$ and 0.01% $Pb(C_2H_3O_2)_2$ was used for platinum black construction and 2 mg/ml dopamine hydrochloride in SPB buffer solution (0.1 mg/mL, 10mM, pH 6.0) was used for polydopamine deposition. Each deposition was conducted in different conditions. For platinum black reduction, 0.5 nA/μm^2 was applied for 2 – 10 seconds and a large gold electrode (1.4 × 2.7 mm^2) was used as a reference electrode. For polydopamine deposition, + 0.5 V was applied for 12 – 30 minutes using a Ag/AgCl (3 M KCl) wire as a reference electrode. Four types of pDA-PtBK microelectrodes were fabricated having different number of layers. Pt-BK microelectrodes were also fabricated for control group. The detailed data are in table 1.

TABLE I. MICROELECTRODE TYPES

Type	Starting layer	Platinum black		polydopamine	
		Layer number	time	Layer number	time
Pt-BK	Pt-BK	1	10 sec	0	
T1	Pt-BK	2	5 sec	2	30 min
T2	pDA				
T3	Pt-BK	5	2 sec	5	12 min
T4	pDA				

Pt-BK: platinum black, pDA: polydopamine

C. Electrical characterization

The impedance of microelectrodes was measured by LCR meter (E4980A, Agilent). The measurement was conducted while a working electrode (microelectrode) and a reference electrode (Ag/AgCl wire) were submerged in phosphate buffered saline. The test signal was 100 mV_{pp} of sine wave and the frequency was ranged from 200 Hz to 100 kHz.

D. Mechanical stability test

The mechanical stability of microelectrodes was tested by measuring impedance values after applying ultrasonication process. The pDA-PtBK and PtBK MEAs were submerged in the ulstrasnoication bath and exposed to sonication shock for 0 to 5 minutes.

III. RESULTS

A. Morphological characteristics

Pt-BK microelectrodes and four types of pDA-PtBK microelectrodes were fabricated and their morphological characteristics were observed by SEM imaging. Fig 1. is representative images of Pt-BK and T4 pDA-PtBK microelectrodes. Both microelectrodes had porous structures but pDA-PtBK had slightly bigger porous size (Fig 1(c) and (f)). The other types of pDA-PtBK microelectrodes had similar structure like T4.

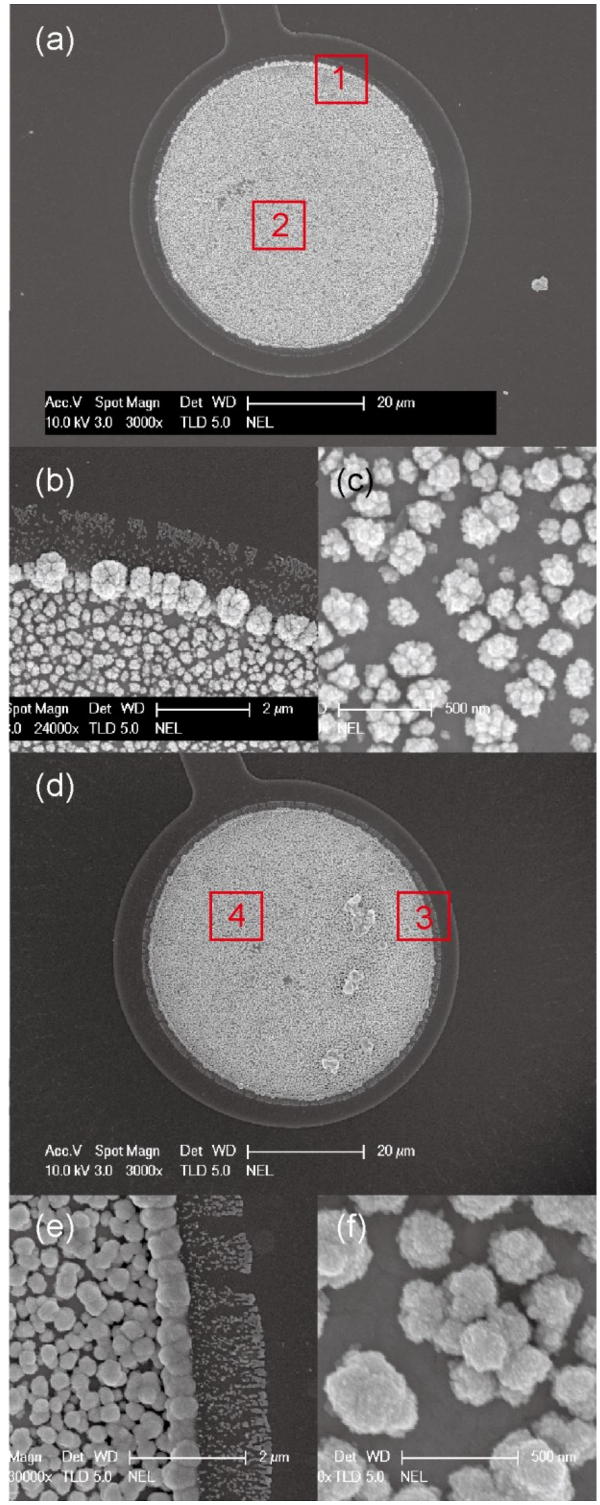

Fig 1. SEM images of Pt-BK (a) and pDA-PtBK microelectrodes (d). (b, c) and (e, f) are enlarged images of 1 and 2 in (a) and 3 and 4 in (d), respectively.

B. Electrical characteristics

The impedance values of each type of microelectrodes were measured (Fig. 2). All data are measured at 1 kHz. The magnitudes of impedances of T1 and T2 pDA-PtBK microelectrode were 28.1 ± 4.69 kΩ and 30.8 ± 21.2 kΩ,

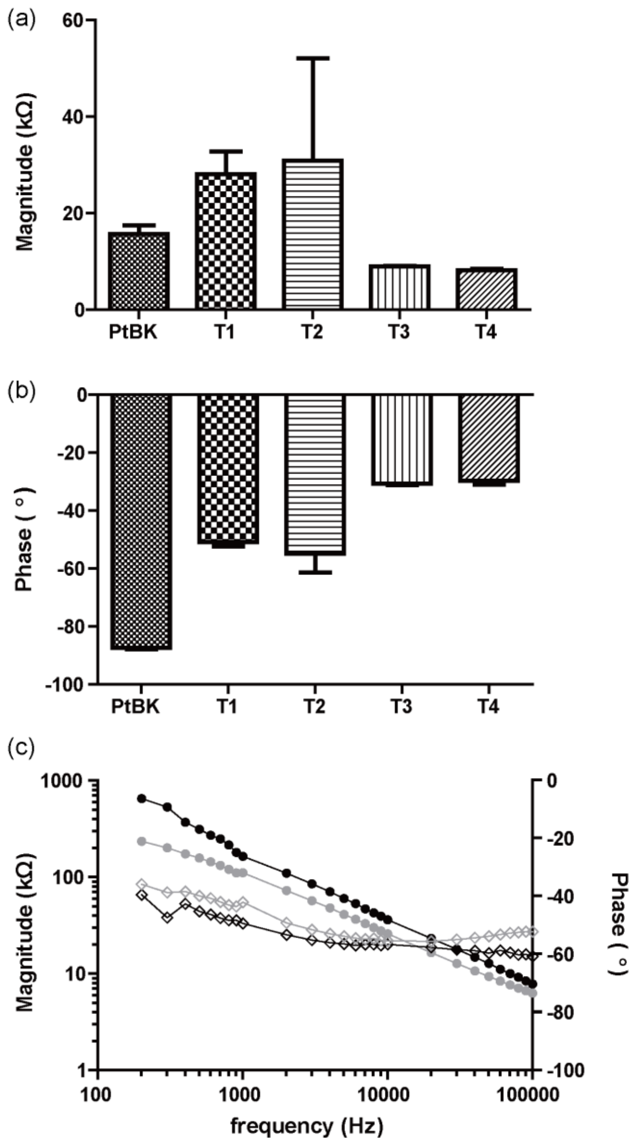

Fig 2. Impedance magnitudes (a) and phases (b) of PtBK and different types of pDA-PtBK microelectrodes. (c) Impedance spectrum of T1 (black) and T3 (grey). Circles and diamonds indicate magnitude and phase, respectively.

respectively and showed a little difference (mean ± s.d, n=25). Likewise, the magnitude values of T3 and T4 pDA-PtBK microelectrode were similar, which were 8.92 ± 0.11 kΩ and 8.20 ± 0.21 kΩ each (mean ± s.d, n=25). These values were comparable to PtBK microelectrode which value was 15.6 ± 1.81 kΩ (mean ± s.d, n=25). The phases of the impedances were increased as the number of polydopamine layer increased. The phase value was increased from -87.6 ± 0.61 ° to -50.9 ± 1.49 °, -54.9 ± 6.46 ° when two polydopamine layers were added and increased up to -30.8 ± 0.45 ° and -29.7 ± 1.38 °(mean ± s.d, n=25) when five polydopamine layers were added. The increment of phase indicates that the electrodes became more resistive.

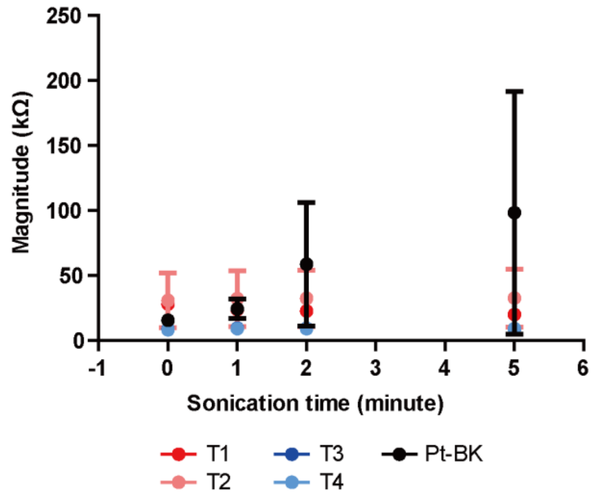

Fig 3. Mechanical stability of PtBK and pDA-PtBK microelectrodes.

C. *Mechanical stability*

Finally, the mechanical stability of microelectrodes were tested (Fig. 3). As a result, the impedance magnitude of PtBK microelectrodes increased from 15.6 ± 1.81 kΩ to 24.2 ± 7.56 kΩ (mean ± s.d, n=25) after one minute of sonication. After five minutes of sonication, the magnitude increased 6.5 times reaching 98.2 ± 93.4 kΩ (mean ± s.d, n=25). The standard deviation value was also increased indicating the each electrode had very different magnitude value. On the other hand, pDA-PtBK microelectrodes showed greatly consistent magnitude values even after the five minutes of sonication. T3 and T4 had almost same magnitude that two data points are overlapped in Fig. 3.

IV. Discussion

The developed pDA-PtBK microelectrodes showed improved mechanical stablity compare to Pt-BK microelectrodes. Polydopamine is known for its adhesive characteristic which strengthen the adhesion between different materials [13,17]. In this study, the polydopamine layers which were placed among platinum black structures might work as a reinforcing agent of platinum black structure. The adhesive property seemed to improve the strength of the brittle platinum black structure. The impedances were maintained at lower level after adding polydopamine layer and the number of polydopamine layer was not a major factor for mechanical stability. The advancement of mechanical property of platinum black microelectrodes will be able to be utilized to develop various neural sensor platform.

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